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Research paper

Polybromide salts of tetraalkyl and N-heterocyclic cations: New entries into the structural library

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ABSTRACT

Reactions between Br_2 dissolved in HBr and salts of various organic cations resulted in formation of a series of polyhalide salts: (IsoquinolH)Br_3 (**1**), (2-BrPyH)Br_3 (**2**), (H_2(4,4′-bipy))(Br_3)$_2$ (**3**), Bu_4NBr_3 (**4**), (Collidinium){(Br_3)(Br_2)} (**5**) and Et_4N{(Br_3)(Br_2)$_2$} (**6**). All compounds were characterized by X-ray diffractometry; the role of supramolecular Br···Br contacts is discussed.

1. Introduction

Polyhalide compounds constitute a field of modern chemistry which attracts much attention [1]. Although the first example of such substances were reported almost 200 years ago [1], new exciting compounds continue to be reported. The most recent results are concentrated on the generation of non-iodide polyhalide units of higher nuclearity (usually more than 5). For example, very recently, Riedel at al. reported formation of stable $[Cl_8]^{2-}$ [2] and a 2D polychloride network [3]. It is known that the tendency to form polyhalide anions decreases dramatically in the row I ≫ Br > Cl > F, and, therefore, polyodides remain the best studied class [4,5].

Interest in polybromides is caused by both fundamental reasons and their potential use in several application areas. In particular, polybromides may be utilized as a form of "capturing" of Br_2 in Zn/Br redox flow batteries, decreasing their ability to spontaneous discharge [6–10]. A number of polybromides with various molecular structures have been reported to date [11–16]; the synthetic approaches towards these compounds may include the use of ionic liquids [17].

During our experiments aiming at the synthesis of novel Bi(III) polybromide complexes [18], we have noticed that in many cases reactions "Br_2 + HBr + $[BiBr_6]^{3-}$" do not lead to the formation of a desired product. Instead, there forms a mixture of bromobismuthate and polybromide (most commonly, tribromide) salts of an organic cation. Considering the fact that XRD and PXRD are the main methods for identification of the products in reactions of this type, information on the crystal structures of such salts is needed to allow their rapid identification. In this work, we describe the crystal structures of six novel polybromides of various organic cations containing different amounts of "captured" dibromine per one Br^-: (IsoquinolH)Br_3 (**1**), (2-BrPyH)Br_3 (**2**), (H_2(4,4′-bipy))(Br_3)$_2$ (**3**), Bu_4NBr_3 (**4**), (Collidinium){(Br_3)(Br_2)} (**5**) and Et_4N{(Br_3)(Br_2)$_2$} (**6**).

2. Experimental section

All reagents were obtained from commercial sources (Sigma-Aldrich) and used without any additional purification. Initially, samples of **1**–**6** were precipitated from the cooled (6 °C) mixtures of two solutions: (1) Bi_2O_3 + excess of Br_2 and (2) bromide of corresponding cation (both in 2 M HBr). Further, the same general approach was applied: solutions of Br_2 and corresponding cation (generated in situ by protonation or taken as bromide salt), both in aqueous 2 M HBr, were mixed together and cooled down to 6 °C.

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